lation was carried out on the basis of an extended Hückel method.[11] Because the donors are arranged almost uniformly along the stacking direction, the intrastack interaction is very strong. On the other hand, interstack overlap integrals are about one third compared to the interstack ones. Thanks to such a relatively strong interstack interaction, the calculated Fermi surface is closed, similar to $(TTP)_2SbF_6$ (Fig. 4), although one-dimensional character is dominant. Further investigations, in particular, the synthesis of the other selenium analogues of TTP are actively in progress.

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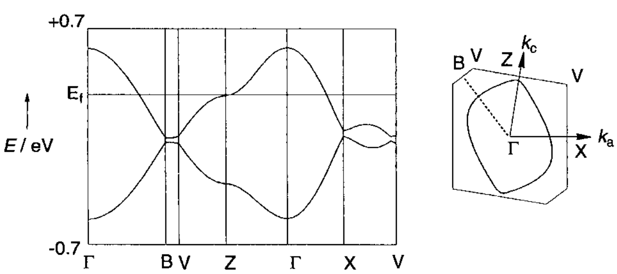

Fig. 4. Energy band structure and Fermi surface of $(ST\text{-}TTP)_2AsF_6$. The intermolecular overlap integrals are $a1 = 21.2$, $a2 = 21.0$, $p1 = 7.5$, $p2 = 5.8$, $c = -0.99 \times 10^{-3}$.

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[10] Crystal data of $(ST\text{-}TTP)_2AsF_6$: $AsC_{20}F_6H_8S_{12}Se_4$, $M = 1137.76$, triclinic, space group $P\bar{1}$, $a = 6.991(2)$ Å, $b = 18.025(4)$ Å, $c = 6.479(2)$ Å. $\alpha = 99.26(2)°$, $\beta = 94.29(2)°$, $\gamma = 81.31(2)°$, $V = 785.5(4)$ Å^3, $Z = 1$, $D_c = 2.405$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 109.38$ cm^{-1}, $F(000) = 543$. The data were collected on a Rigaku AFC7R diffractometer equipped with graphite monochromated Mo Kα radiation using the ω–2θ scan technique to a maximum 2θ of 55°. The structure was solved by direct methods and refined by full-matrix least squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.047$, $R_w = 0.054$ for 2213 observed ($I \geq 3\sigma(I)$) reflections from 3616 unique data. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation. Further details of the crystal structure investigation may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on quoting the full journal citation.
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Surfactant-Assisted Self-Organization of Cobalt Nanoparticles in a Magnetic Fluid

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Stable dispersions of single-domain magnetic nanoparticles in either organic or inorganic solvents are called magnetic fluids. Ferromagnetic colloids, often called ferrofluids, are of immense technological importance.[1–3] They have been used as magnetic seals in motors and devices such as gas lasers, blowers, etc., and as lubricants and bearings in magnetic disk drive spindles, optical memory devices, and gyroscopes. Other applications are in magnetic devices such as stereo speakers, magnetic inks for bank checks, magnetic refrigeration units, etc. Ferrofluids also find application in medicine, for example, in drug delivery, restriction of blood flow to a selected part of the body, and act as opaque materials for diagnostic imaging using X-ray or nuclear magnetic resonance (NMR). The various applications are summarized in a review article by Raj and Moskowitz.[1]

Magnetic fluids containing fine particles of ferromagnetic metals such as cobalt and iron have higher performance than the currently used magnetic fluids containing fine particles of magnetite and other ferrite materials because of their much higher saturation magnetization compared to magnetite or ferrites. The stabilization of these magnetic fluids can be achieved by coating the particles with long-chain surfactant molecules such as lauric acid, oleic acid, poly(vinyl)amine and the double surfactant layers.[4] The role of the surfactant here is to produce the entropic repulsion needed to overcome the strong short-range van der Waals attraction that otherwise results in irreversible particle aggregation and the consequent colloidal instability that leads to precipitation. Stearic acid cannot be used to form a stable colloid, unlike oleic acid, which has a double bond. The reason is the kink caused by the double bond in oleic acid, which inhibits the neighboring chains from bundling together.[5,6] However, lauric acid, which has a short chain of 12 carbons all joined by single bonds, behaves like a long-chain unsaturated oleic acid. This leads to the open question, what is the driving mechanism for the stability of these colloids by various surfactants?

There is strong evidence, from both theoretical[7] and experimental[8–10] work, that, in the presence of a magnetic field, chaining and aggregation of particles occur. The pro-

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cess normally appears to be reversible on removal of the field, provided the field is weak.[11] Rosensweig has studied in detail the organizational effect and the pattern formations in magnetic fluids under an applied magnetic field.[6] Nikles and co-workers have prepared spherical as well as acicular α-Fe particles by the reduction of a low concentration of Fe^{2+} ions with $NaBH_4$ in a tubular lecithin/cyclohexane/water reverse micelle solution under an applied magnetic field of 1200 Oe.[9] Further, they observed that the yield of the acicular particles can be increased in the presence of an association colloid, a $C_{12}EO_4$/water lamellar liquid-crystalline phase.[10] $C_{12}EO_4$ is a non-ionic surfactant with the chemical formula $C_{12}H_{25}(OCH_2CH_2)_4OH$. This clearly shows the role of colloidal systems in the formation of acicular particles.

However, reports on the self-organization of magnetic particles in the absence of a magnetic field are scanty. Matijevic et al.[12] have synthesized spindle-shaped colloidal hematite (α-Fe_2O_3) particles of narrow size distribution by forced hydrolysis of $FeCl_3$ solution at elevated temperatures. It was shown that the addition of small quantities of phosphate or hypophosphate ions to such systems before aging has a significant effect on the resulting particle shape. This observation was attributed to surface interactions of phosphate ions with nuclei influencing the subsequent growth mechanism, resulting in anisometric particles. Ocana et al.[13] have also reported the preparation of nanocrystalline acicular hematite particles by aging $FeCl_3$ solutions at 100 °C in the presence of phosphate anions. Polymer-stabilized colloidal Co particles of face-centered cubic (fcc) structure had been prepared earlier by thermal decomposition of the solution of precursor, dicobalt octacarbonyl, $Co_2(CO)_8$, in hydrocarbon solvents containing suitable polymeric materials.[14,15]

In this paper, we describe the preparation, growth, and the stability of amorphous cobalt nanoparticles in a surfactant-stabilized colloidal solution. In earlier studies, we showed the high reactivity of the amorphous iron nanoparticles towards surfactants such as long-chain thiols[16] and alkyl trichlorosilanes.[17] The magnetic colloid was prepared by ultrasonic decomposition of the volatile precursor, $Co(NO)(CO)_3$, solution in decane in the presence of a stabilizing agent, oleic acid (octadec-9-ene-1-carboxylic acid).

The precursor $Co(NO)(CO)_3$ was prepared by the known method.[18] A decane solution of 0.25 M $Co(NO)(CO)_3$ and 0.04 M oleic acid was sonicated at 273 K for 3 h, under an argon pressure of 100–150 kPa, using a high-intensity ultrasonic probe (Sonics and Materials, Model VC-600, 1.25 cm Ti horn, 20 kHz, 100 W cm^{-2}). The resulting black solution was heated at 50 °C under vacuum to remove any unreacted $Co(NO)(CO)_3$ and then transferred to a glove box for further studies. The colloidal solution was stable for two months and no precipitation was observed. Transmission electron microscopy (TEM) was carried out by placing 1 or 2 drops of the colloidal solution onto a Formvar-coated copper grid (200 mesh) and drying it. The Fourier transform infrared (FTIR) spectra of the evaporated residue of the aged (one month) colloid was recorded on a Nicolet FTIR spectrometer by mixing the sample with spectroscopic grade KBr in the ratio 1:50. Magnetic data of the as-prepared colloidal solution at 200 K (frozen state) were obtained with a magnetometer based on a superconducting quantum interference device (SQUID). The magnetization loops were measured at room temperature for the evaporated residue of the aged colloidal solution.

TEM bright field images were taken after different aging periods, for example, of fresh (10 min of sonication time), one week old, and one month old colloidal solutions. Figure 1a shows the spherical cobalt particles of about 5–10 nm size obtained in the freshly prepared colloidal solution. With time, the particles try to self-organize in a peculiar way in the presence of the surfactant oleic acid. After a week of aging, these small nanosized particles of cobalt are observed in different states of aggregation (Fig. 1b). The ordered growth proceeds until a uniform acicular- (ellipsoi-

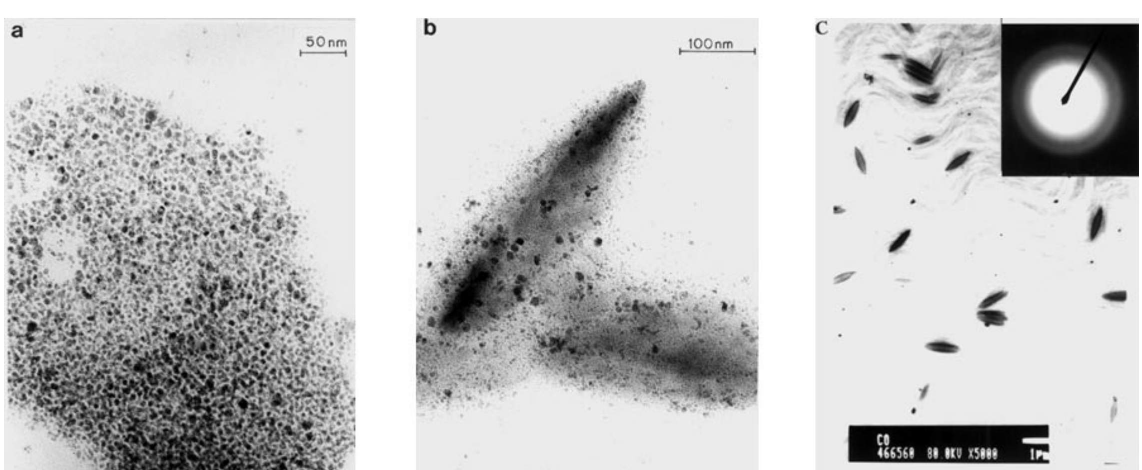


Fig. 1. TEM micrographs of the cobalt colloidal solution: a) as prepared fresh, b) after a week of aging, c) after a month of aging (inset: ED pattern).

dal-) shaped particle of about 1 μm size with an aspect ratio of 5:1 is reached for a month old colloidal solution (Fig. 1c). The TEM-EDX (EDX: energy dispersive X-ray) profile of these particles gave over 99 % of cobalt with other trace impurities as adsorbed materials. The electron diffraction pattern (Fig. 1c, inset) showed diffuse rings, clearly indicating the amorphous nature of this sample. A schematic diagram of the mechanism proposed is depicted in Scheme 1.

We believe that the primary particles formed are spherical in shape, and the interparticle collisions, which happen at very high speed during high-intensity ultrasound radiation, ultimately leads to agglomeration, changing the morphology of the particles.[19] This facilitates the adsorption of the oleic acid on a plane perpendicular to the long axis of the now elliptical cobalt nanoparticles. Such a kind of preferential adsorption of the phosphates on the planes parallel to the *c*-axis has been observed in hematite nuclei.[13,20] This preferential adsorption of the surfactant inhibits the sideways interconnection of the particles, which results in further aggregation of the particles in an ordered manner, thus leading to the growth of acicular particles.

The magnetic dipole–dipole interaction plays an important role[21] in forming elongated particles. This force is more significant when particles become longer, since the magnetic moment of such particles increases due to an increase of the shape anisotropy. The magnetization loop of freshly prepared colloidal solution, measured at 200 K, is depicted in Figure 2a. The data show no hysteresis and no saturation magnetization up to a magnetic field of 22 kG. The lack of saturation in magnetization as well as the absence of an hysteresis is the indication of the superparamagnetic behavior that is typical for the assembly of single-domain nanoparticles of ferromagnetic materials. Surprisingly, when the experiment was repeated on a month-old colloidal solution, no appreciable signal for magnetization was detected by SQUID (within the instrumental limitations). This reduction in magnetization for the acicular cobalt particles in an aged colloidal solution is naturally explained by the dramatic increase of the magnetic shape anisotropy in these particles. As magnetization measurements are conducted on a frozen colloid, where the magnetic easy axes are distributed randomly and the particles are immobile, one expects a decrease in the total magnetic moment measured in the direction of the applied field.[21]

The vibrating sample magnetometer (VSM) data of the evaporated residue of the month-old colloid (Fig. 2b)

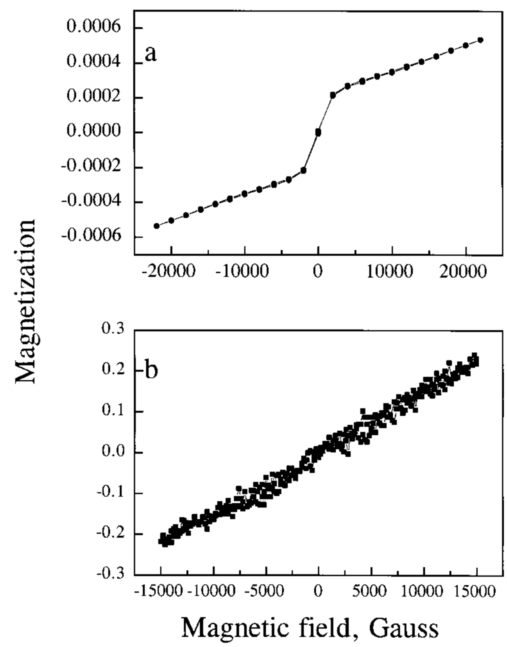
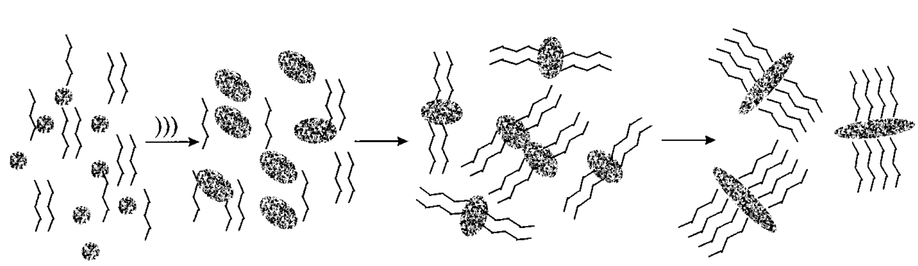


Fig. 2. Magnetization loops of the cobalt particles in: a) as-prepared fresh colloidal solution, b) evaporated residue of the one-month aged colloidal solution.

showed no ferromagnetic behavior. The aggregation of the superparamagnetic particles into acicular shape, as described previously, is most likely owing to long-range dipole–dipole interactions, whereas ferromagnetic ordering requires short-range exchange interactions. Indeed, it may happen that the particles come close enough to each other so that exchange interaction between them becomes important. Still, the assembly of resulting elongated aggregates will exhibit superparamagnetic properties, because the creation of the magnetic domain inside such elongated particles is still unfavorable due to the unchanged small transverse size. The role of surfactant here is to assist the unidirectional growth by inhibiting the side interconnection of the magnetic particles.

The string formation of Co nanoparticles (20 nm sized) in a copolymer-stabilized colloidal solution has been reported earlier.[14,15] Magnetic properties of these particle assemblies, measured on dried films formed by the evaporation of the solvents with polymer materials acting as binders, implied that the particles were monodomain.[15] The loss of ferromagnetism for the evaporated residue of



Scheme 1.

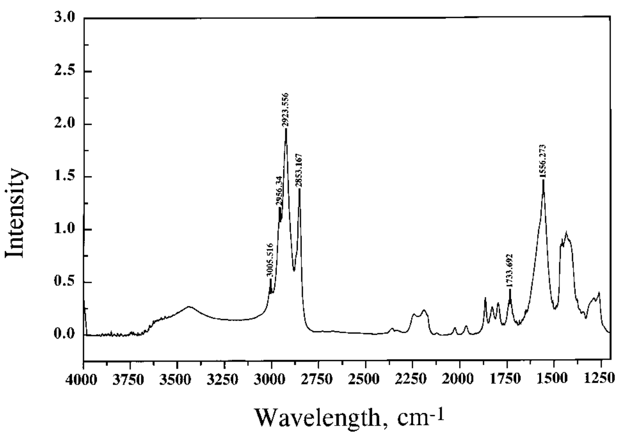


Fig. 3. FTIR spectrum of the evaporated residue of the aged cobalt colloidal solution.

our colloid can also be attributed to the strong interaction between the surfactant, oleic acid, and the cobalt nanoparticles, taking into account the high reactivity of these nanosized amorphous metallic particles.[16,17] FTIR studies (Fig. 3) clearly indicate that the surfactant, oleic acid, is strongly bound to the cobalt particles, predominantly in oleate form, and the free acid present is also physisorbed on the surface. The strong absorption bands in the CH_2 stretching region, 2853 cm^{-1} (symmetric) and 2923 cm^{-1} (asymmetric), clearly indicate the presence of surfactants on the cobalt surface.[22,23] The CH_3 asymmetric stretching vibration is also seen at 2956 cm^{-1} and the one at 3005 cm^{-1} is the olefinic CH stretch. The strong band at 1556 cm^{-1}, in the asymmetric region, indicates the presence of adsorbed oleate anions. The weak to medium band at 1733 cm^{-1} shows the presence of adsorbed monomeric oleic acid as well.[24]

In conclusion, the dramatic reduction of the measured magnetization of the aged colloid is explained to be due to an increase of the magnetic shape anisotropy of the elongated particles. The role of surfactant is to stabilize the unidirectional growth, in the sense that surfactant inhibits the side interconnection of the magnetic particles. We are now in the process of investigating the kinetics of oleate formation and the reactivity of amorphous cobalt nanoparticles towards various other surfactants.

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A New Blue Light-Emitting Polymer Containing Substituted Thiophene and an Arylene-1,3,4-oxadiazole Moiety

By *Wei Huang*,* *Hong Meng*, *Wang-Lin Yu*, *Jun Gao*, and *Alan J. Heeger*

Conjugated polymers have attracted intensive attention in the past twenty years on account of their unique electrical and optical properties.[1] Their application as light-emitting materials has resulted in a new kind of electroluminescent devices—polymer light-emitting diodes (PLEDs),[2,3] which have shown many advantages over conventional electroluminescent devices. Poly(*p*-phenylenevinylene) (PPV),[4] polythiophenes (PT),[5] poly(*p*-phenylene) (PPP),[6] and polyfluorene (PF)[7] are widely used conjugated polymers in PLEDs. The electroluminescence (EL) from these polymers can sweep the whole range of the visible spectrum. However, all these polymers have a π-excessive nature, i.e., they are typical p-doped type polymers with much greater tendency for transporting holes than for transporting electrons. This charge imbalance is one of the key limits to increasing the EL quantum efficiency of PLEDs. Although the EL quantum efficiency of PLEDs may be increased greatly by adding charge injection/transporting layers between a light-emitting polymer film and the electrodes,[8] synthesis of light-emitting polymers with strong electron affinity is necessary for fabricating highly

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